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XII. "On the Peroxides of the Radicals of the Organic Acids."

By Sir B. C. BRONIE, Bart., Professor of Chemistry in the University of Oxford. Received June 18, 1863.

(Abstract.)

In a former notice published in the 'Proceedings of the Royal Society' (vol. ix. p. 361), an announcement was made of the discovery of a new group of organic combinations, the peroxides of the radicals of the organic acids—bodies which in the systems of the combinations of these radicals occupy the same relative position as is held by the peroxides of hydrogen, barium, or manganese in the systems of the combinations of those elements. An account was given of the mode of preparation and properties of two members of this group, the peroxides of benzoyl and of acetyl, $C_{14}H_{10}O_4$ and $C_4H_6O_4$. The present paper contains an extension of this inquiry. In it is given an account of several other peroxides of monatomic radicals, the peroxides of nitro-benzoyl, of cumenyl, of butyl, and of valeryl, and also an inquiry into the action of the peroxide of barium on the bibasic anhydrides.

The nitro-benzoic peroxide is formed by the action of fuming nitric acid on the peroxide of benzoyl. It stands to peroxide of benzoyl in the same relation as anhydrous nitro-benzoic acid stands to anhydrous benzoic acid, and may be regarded as derived from that peroxide by the substitution in it of two atoms of peroxide of nitrogen for two of hydrogen. The formula of the substance is $C_{14}H_8(NO_2)_2O_4$.

			Calculated.		Found.
C ₁₄	168	50.60	50.60
H ₈	8	2.41	2.58
N ₂	28	8.43	8.49
O ₈	128	38.56	38.33
	<u>332</u>		<u>100.00</u>		<u>100.00</u>

The peroxide of cumenyl is procured by a process strictly analogous to that by which the peroxide of benzoyl is formed; it has the constitution $C_{20}H_{22}O_4$.

The peroxides of butyl and valeryl are prepared by the action of hydrated peroxide of barium on the anhydrous acid. It is only necessary to mix in a mortar equivalent quantities of the two sub-

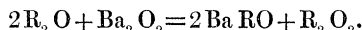
stances. The peroxide is separated by solution in ether from the water in which it is dissolved and suspended. These substances are dense oily fluids, exploding slightly when heated, but not so readily decomposable as the peroxide of acetyl. The analysis of the peroxide of butyl, dried by chloride of calcium, gave results corresponding with the formula $C_8H_{14}O_4$.

			Calculated.		Found.
C ₈	96	55.17	55.11
H ₁₄	14	8.05	8.28
O ₄	64	36.78	36.61
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		174		100.00	100.00

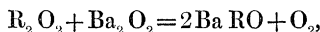
The analysis of the peroxide of valeryl gave results corresponding with the formula $C_{10}H_{18}O_4$.

				Calculated.		Found.
C_{10}	120	59.40	59.39
H_{18}	18	8.91	9.17
O_4	64	31.69	31.44
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		202		100.00		100.00

The mode of formation of these peroxides is given in the equation



These substances are decomposed as well as formed by the action of the alkaline peroxide, according to the equation



giving a striking example of those consecutive actions referred to in a former paper as the cause of certain catalytic decompositions.

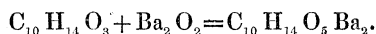
The action of the bibasic anhydrides on the alkaline peroxides is of special interest.

When anhydrous succinic acid, lactide, or anhydrous camphoric acid is mixed with an equivalent of hydrated peroxide of barium, a solution is obtained possessing the most powerful oxidizing properties, which bleaches indigo, evolves chlorine with hydrochloric acid, and oxidizes the protosalts of iron and manganese, but which does not discolour permanganic acid, or give with chromic acid the blue colour formed by peroxide of hydrogen. When boiled, the solutions evolve oxygen, and afterwards contain a salt of the acid employed—in the case of succinic acid, giving a crystalline precipitate of succinate of

barium, and in the case of camphoric acid, giving with acetate of lead a precipitate of camphorate of lead. These solutions are in a state of continual decomposition. Only in one instance, that of camphoric acid, was it found possible to analyse the substance, and that only by indirect processes. The oxygen contained in the organic peroxide was estimated in a measured portion of the solution by means of a standard solution of iodine; the camphoric acid formed on boiling was determined by precipitation with acetate of lead in another measured portion; and in a third portion the barium was estimated as sulphate. The results of these determinations are given below, the camphoric acid being assumed as correct. They lead to the conclusion that the solution contains the elements of one equivalent of anhydrous camphoric acid, one of oxygen, and one of baryta.

	Atomic weight.	Calculated ratio.	Found.
$C_{10}H_{14}O_3$	182	25·12	25·12
O	16	2·20	2·07
Ba_2O	153	21·12	21·51

the reaction being



That the substance formed is to be regarded as the baryta salt of the peroxide of camphoryl, and not as the camphorate of the peroxide of barium, is proved by the reactions of the solution, which does not give peroxide of hydrogen when decomposed by acids, or a precipitate of the hydrated peroxide of barium when heated with a solution of baryta.

The organic peroxides constitute a new and peculiar group of chemical substances characterized by reactions never hitherto found in any compound of carbon, and which materially extend our views of the possible properties of the so-called organic combinations, and of their analogies to inorganic substances. They are the organic representatives of chlorine in the same sense as the oxides of the compound ammoniums are the representatives of potash, and in a yet closer sense than ether and alcohol resemble the oxide and its hydrate, or than ethyl or marsh-gas are analogous to hydrogen. This analogy is of a profound character, not consisting merely in the analogy of symbolic form, but in the absolute identity of reactions.

The admitted analogies of the peroxide of chlorine have as it were their maximum in the organic peroxide. Not only is chlorine represented in the peroxide, but hydrochloric acid is represented in the organic acid, and a series of parallel equations may readily be constructed, showing the identical character of the reactions of the two classes of substances. Both bleach a solution of indigo, oxidize the protosalts of iron and manganese, decompose water under the influence of sunlight, and evolve oxygen with an alkaline peroxide, forming the salt of the corresponding acid.

XIII. "Explorations in Spitzbergen, undertaken by the Swedish Expedition in 1861, with the view of ascertaining the practicability of the measurement of an Arc of the Meridian." By Dr. OTTO TORELL, Professor of Zoology in the University of Lund. Communicated by the President. Received June 2nd, 1863.

In the year 1858 I made a voyage to Spitzbergen, in company with two other naturalists, in order to investigate the Natural History of that country.

I was thereby induced to study the history of the various Arctic expeditions that had gone out from England.

In Beechey's and Barrow's works I saw mentioned a suggestion which attracted my attention in a high degree. A letter is there given from Captain Edward Sabine to Mr. Davies Gilbert, in which the writer, on his return from his celebrated Pendulum Expedition, proposes to explore Spitzbergen, with the view of ascertaining whether the measurement of an arc of the meridian could be carried out there*.

An arc from Ross Islet to Hope Island would comprise nearly $4\frac{1}{2}^{\circ}$ of latitude—equivalent to an arc of 9° in the mean latitude of France, and of 7° in the mean latitude of Great Britain.

The difficulties opposed by climate and ground were not considered by Captain Sabine to be so great as not to be surmounted; and he offered, in company with another officer and a sergeant of

* Quarterly Journal of the Royal Institution, vol. xxi. art. xi. pp. 101-108.